Optical Properties and Emissivities
of Liquid Metals and Alloys

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Abstract

This paper presents the results from our on-going program to investigate the optical properties of liquid metals and alloys at elevated temperatures. Ellipsometric and polarimetric techniques have been used to investigate the optical properties of materials in the 1000 - 3000 K temperature range and in the 0.3 - 0.1 μm wavelength range. The ellipsometric and polarimetric techniques are described and the characteristics of the instruments are presented.

The measurements are conducted by reflecting a polarized laser beam from an electromagnetically levitated liquid metal or alloy specimen. A Rotating Analyzer Ellipsometer (RAE) or a four-detector Division-of-Amplitude Photopolarimeter (DOAP) is used to determine the polarimetric properties of the light reflected at an angle of incidence of approximately 68°. Optical properties of the specimen which are calculated from these measurements include the index of refraction, extinction coefficient, normal spectral emissivity, and spectral hemispherical emissivity. These properties have been determined at various wavelengths and temperatures for liquid Ag, Al, Au, Cu, Nb, Ni, Pd, Pt, Si, Ti, Ti-Al alloys, U, and Zr.

We also describe new experiments using pulsed-dye laser spectroscopic ellipsometery for studies of the wavelength dependence of the emissivities and optical properties of materials at high temperature. Preliminary results are given for liquid Al.

The application of four-detector polarimetry for rapid determination of surface emissivity and true temperature is also described. Characteristics of these devices are presented. An example of the accuracy of this instrument in measurements of the melting point of zirconium is illustrated.

Outline

I.   Introduction
> The Need for Predictive Theories for Liquids
> Experimental and Theoretical Plan

II.   Optical Property Measurements on Liquids
> Rotating Analyzer Ellipsometry
> Emissivity vs temperature measurements
> Optical properties of Zr and U

III.   New Experiments in Progress
> Pulsed Dye Laser Spectroscopic Ellipsometry
> Preliminary Results on Liquid Aluminum
> Total Hemispherical Emissivity

IV.   Applications: Four Detector Polarimetry
> Requirements
> Method
> Device
> Specifications

V.   Melting Point of Zirconium

INTRODUCTION

Predictive models for liquid metals are unavailable due to the lack of accurate experimental data for high temperature liquids. These measurements show:

o   Cp >> 3R, anharmonic terms and electronic contributions are important.

o   Errors in T measurement due to emissivity dependence on temperature. Properties that are derivatives w.r.t. temperature may be in substantial error.

o   Resistivity, volume expansion as a function of T show non-linearities.

o   Electronic structure of simple low-melting liquid metals (s and p electron) dominated by free carrier absorption show good agreement with the nearly-free electron theories. However, transition metals cannot be modelled with the NFE. They also react with containers at high T. Containerless measurements of the optical properties and electronic structure of liquids is a great opportunity to advance our fundamental understanding of the liquid state.

SCIENTIFIC OBJECTIVES

o   To obtain experimental data for the determination of the electronic properties and the electronic density of states of high temperature liquids above and below the MP.

o   To obtain optical property data at high temperatures on liquid metals and alloys above and below the melting point over a wide wavelength range (0.1-15 eV). Practically, we can do 0.25-5.8 eV (5000 - 220 nm).

o   To promote the development of predictive theories for liquid metals and alloys. These theories require additional thermophysical property measurements and accurate temperature measurements.

The plan to develop predictive theories for liquid metals:

Experimental considerations:

1. Accurate experimental data on liquid metal electronic, thermal and optical properties. These include C_p, densities, surface tensions, and electronic properties.
    *   Thermal and transport.
    *   Mechanical and transport.
    *   Electronic and optical properties.

2. Structure factor measurements (Radial distribution functions, coordination numbers, defects): Preliminary studies leading to neutron diffraction and scattering experiments on levitated liquid metals are in progress.(Mary-Louise Saboungi, Argonne)

3. Pair potentials for pure elements. Partial pair correlation functions for alloys. These can be calculated from measured radial distribution functions. (W. Johnson, Caltech)

4. These results will be the basis for analytical modelling and theoretical development work. (S. A. Rice, Univ. Chicago)

Theoretical considerations:

1. The d-bands lie below the s-p bands for simple metals and Orthogonalized-Plane-Wave (OPW) techniques work well for calculating electronic structures.

2. Transition metals - W.A. Harrison has determined the OPW form factors for simple metals. He extended the method to metals where d-bands overlap the Fermi level and are hybridized with s-p bands.

3. Optical property data in the UV, visible, and IR spectral regions are required to determine the electronic structure.
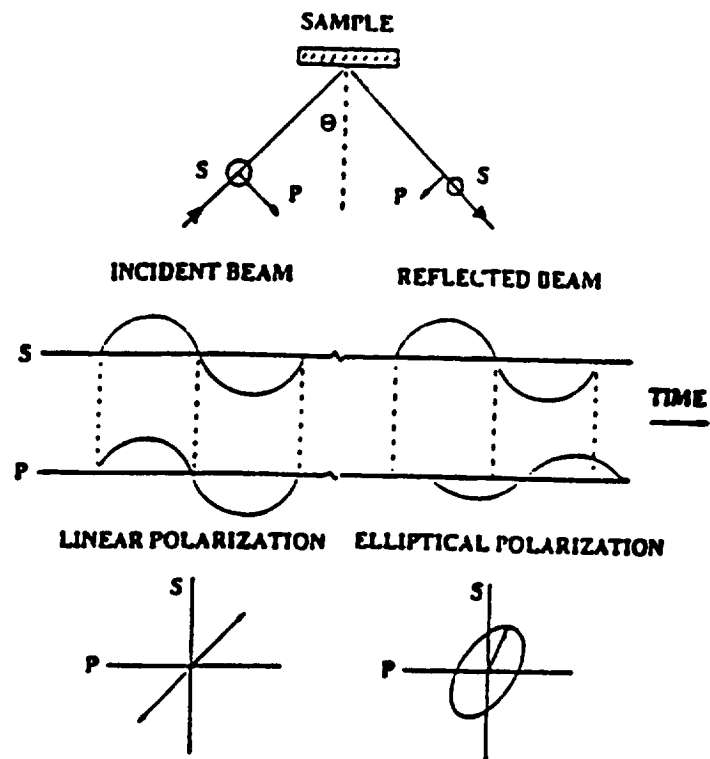
SAMPLE

Θ

S ⊘ P   P ⊘ S

INCIDENT BEAM   REFLECTED BEAM

S

TIME

P

LINEAR POLARIZATION   ELLIPTICAL POLARIZATION

S   S

P   P

Figure 4-1. Illustration of change in amplitude and phase of reflected light.

SAMPLE

REFLECTED BEAM
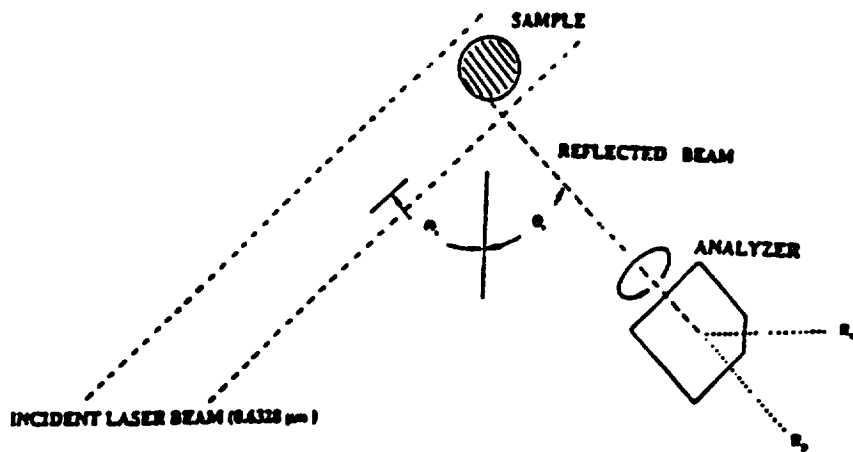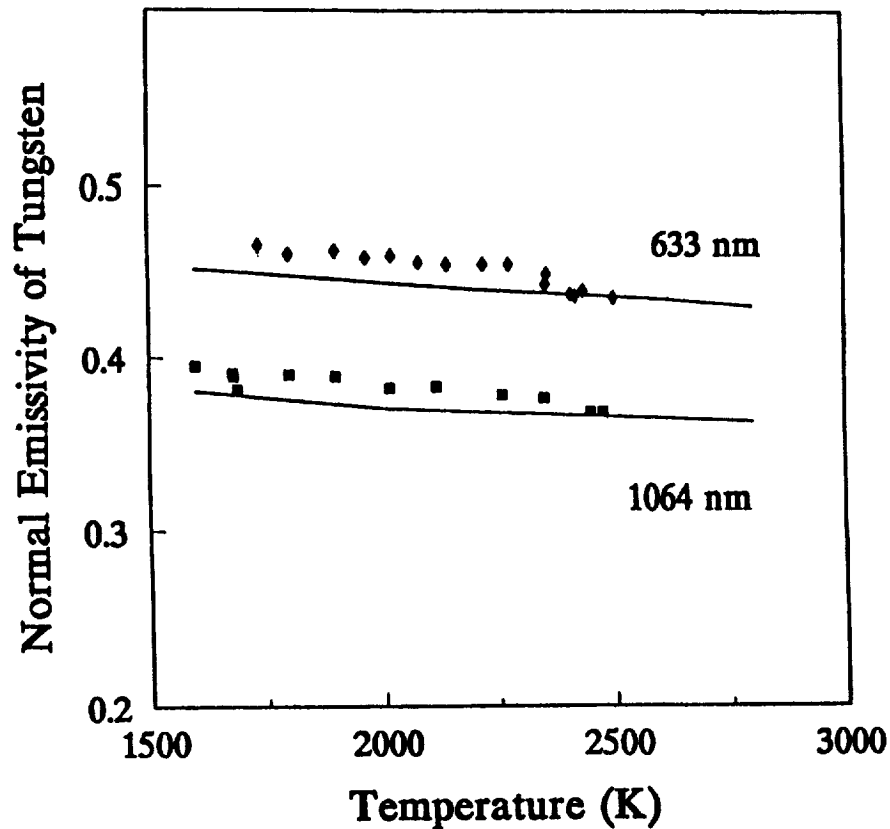
ANALYZER

INCIDENT LASER BEAM (0.6328 μm)

Illustration of Rotating Analyzer Ellipsometry

Optical properties and emissivities have been determined for liquid uranium and zirconium in the temperature ranges:

Uranium: 2000 - 2800K
Zirconium: 2000 - 2700K

Results will be published in:

S. Krishnan, J. K. R. Weber, C. D. Anderson, P. C. Nordine, and R. I. Sheldon, "Spectral Emissivity and Optical Properties at $\lambda = 632.8$ nm for Liquid Uranium and Zirconium at High Temperatures," to be published, J. Nuclear Materials

Spectral emissivity of liquid metals near
their melting points measured by laser polarimetry

Element	Melting Point (K)	Measurement Temperature (K)	Normal Spectral Emissivity Wavelength, (nm): 488	514.5	632.8	1064
Ag	1234	1300	0.11	0.05	0.09	0.06
Al	933	1000			0.04	
Au	1386	1400	0.52	0.47	0.30	0.12
Cu	1357	1400	0.45	0.30	0.13	0.09
Nb	2750	2750			0.32	
Ni	1726	1800	0.49	0.41	0.40	0.31
Pd	1825	1925	0.47	0.38	0.38	0.23
Pt	2045	2250	0.48	0.45	0.38	0.30
Si	1761	1761			0.19	
Ti	1946	1946			0.31	
U	1405	2200			0.28	
Zr	2125	2125			0.35	

Emissivities from laser polarimetry at λ =
632.8 nm and the literature at λ = 645-665 nm for
liquid metals near their melting points.

Element	Normal spectral emissivity Polarimetry	Literature (Ref.)
Ag	0.09	0.08 (29) 0.09 (30,31)
Al	0.04	
Au	0.30	0.31 (30) 0.22 (32)
Cu	0.13	0.13 (30) 0.14 (29)
		0.11 (33)
Nb	0.32	0.32 (29) 0.34 (34)
Ni	0.40	0.39 (29) 0.38 (35)
Pd	0.38	0.37 (32) 0.37 (36)
Pt	0.38	0.38 (32) 0.39 (37,38)
Si	0.19	0.22 (39)
Ti	0.31	0.43 (29) 0.40 (40)
U	0.28	0.32 (41)
Zr	0.35	0.367 ( )

AUTOMATED ROTATING ANALYZER ELLIPSOMETRY:

Instrument design:

o   Tunable pulsed dye laser

o   Fully automated ellipsometer, including rotation, data acquisition, and alignment

o   Automatic scanning of laser wavelength

o   Achromatic design from 0.22 - 0.95 μm:
- Calcite polarizers
- Silicon photodiodes
- Silica lenses

o   Spectral emissivity and optical properties may be measured as rapidly as 1 every second per wavelength.

Infrared instrument design:

o   YAG pumped Infrared Parametric Oscillator (IPO) for 1-4.5 μm

o   Phase-matched, sum-difference non-linear KTP system.

o   Continuous tuning from 1-4 μm with energies > 5 mJ/ 7 ns pulse.

o   Achromatic ellipsometer components and design for 1 - 7 μm
- Rutile polarizers
- PbS, InAs detectors
- CaF_2 lenses and optics, gold mirrors

Method:

A brief summary of the method is outlined here. Light, plane-polarized with an initial azimuth, Ψ_0 to the plane of incidence, is reflected from a metal surface. The P (parallel) and S (perpendicular) components of the incident electric vector experience different phase changes and different reflectivities producing a new azimuth Ψ . If Ψ_0 = 45°, and the reflected light intensity is measured at four azimuths of a rotating analyzer, I_1 (90°), I_2 (0°), I_3 (45°), and I_4 (135°), then the fundamental ellipsometric parameters, Ψ , and Δ , are given by:
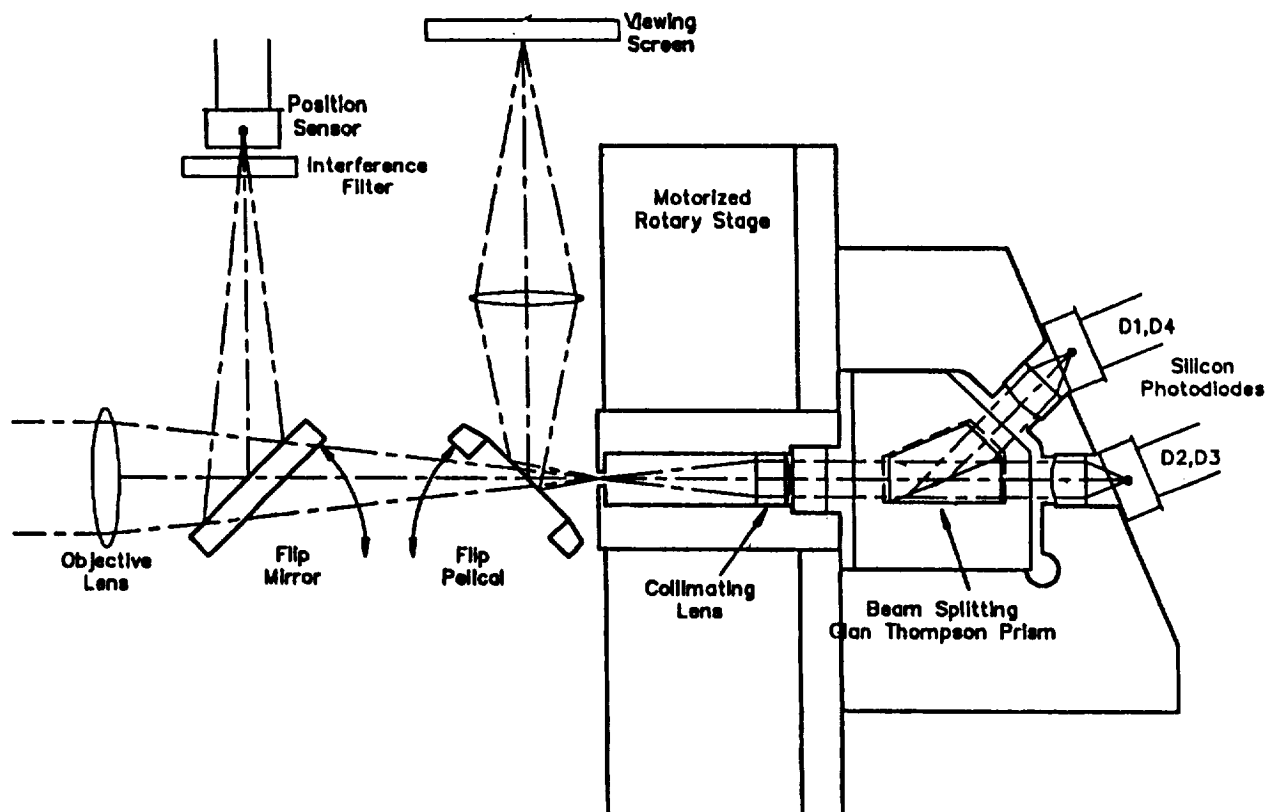
$$\tan (\psi) = \sqrt{\frac{I_2}{I_1}}$$

(22)e

$$\cos (\Delta) = \frac{1}{2}\left[\sqrt{\frac{I_2}{I_1}} + \sqrt{\frac{I_1}{I_2}} \right] \times \left[\frac{1 - \frac{I_4}{I_3}}{1 + \frac{I_4}{I_3}} \right]$$

(23)

Instrument for Optical Property Measurements
Wavelength Range: 0.2 to 1.0 um
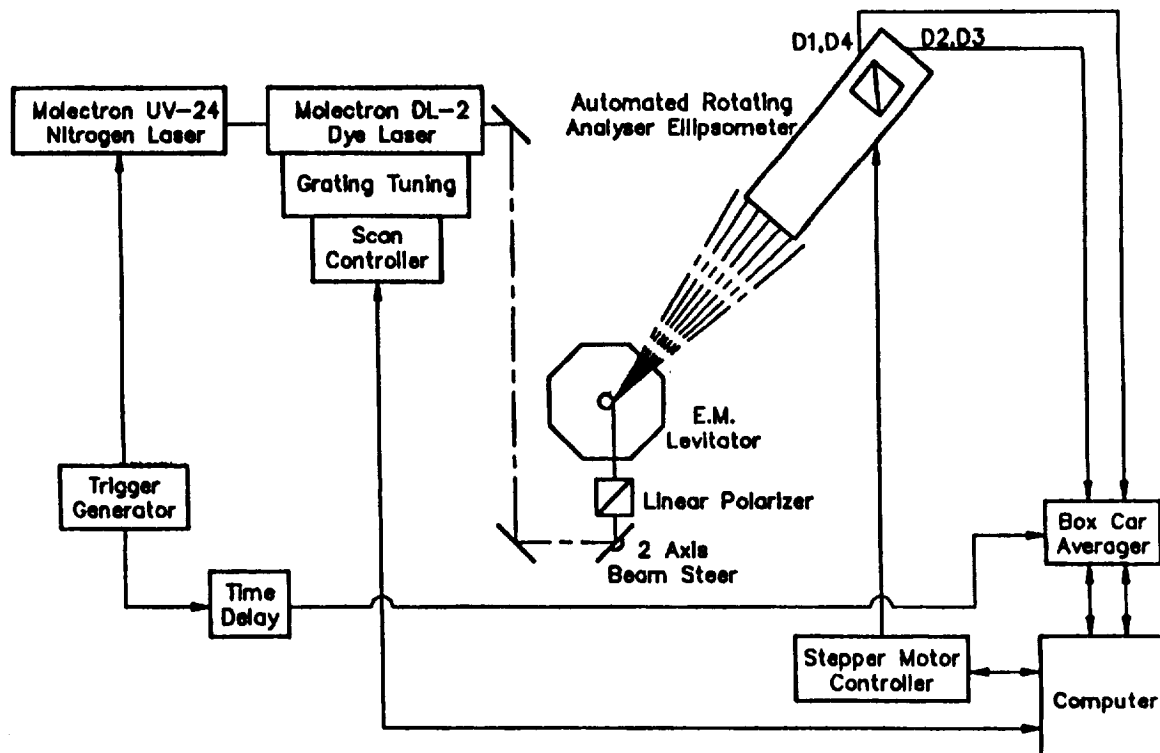
SPECTROSCOPIC AUTOMATED ROTATING ANALYSER ELLIPSOMETER

Spectroscopic Optical Properties
of Clean Liquid Aluminum

Preliminary optical property and emissivity measurements on liquid aluminum have been completed at:

Temperature range   1200 - 1600K
870   1200-1600
Wavelength range   360 - 990 nm

Photon energy range   1.2 - 3.2 ev

Determination of Total Hemispherical Emissivities

Total emissivity is determined from spectral hemispherical emissivity data by integration over the wavelength range for Planck's radiation.

$$\epsilon_{t,h}(T) = \frac{\int_0^\infty I_{bb}(\lambda, T)\, \epsilon_{s,h}(\lambda, T)\, d\lambda}{\int_0^\infty I_{bb}(\lambda, T)\, d\lambda}$$

The denominator of this equation is given by the Stefan-Boltzmann law:

$$\sigma\, T^4 = \int_0^\infty I_{bb}(\lambda, T)\, d\lambda$$

In practice it is necessary to have spectral hemispherical emissivity data over the majority of the wavelength range in which Planck's radiation is emitted:

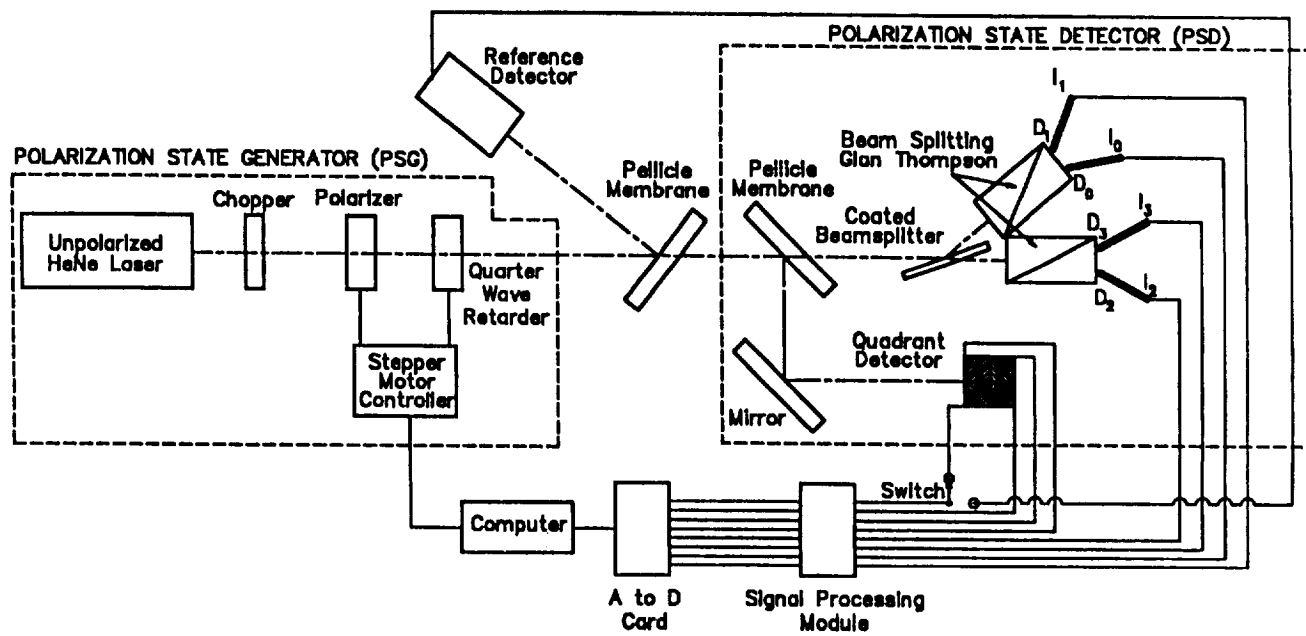| Fraction of Planck's radiation	Wavelength-temperature limits
5% to 95%	$1.88 \times 10^3 - 1.25 \times 10^4$ μm K
10% to 90%	$1.45 \times 10^3 - 9.37 \times 10^3$ μm K

In practice, the spectral emissivities are small in the infrared so that, by the previous equation, the longer wavelength limit of integration can be reduced. Using 5% to 90% limits, the wavelength vs temperature requirements are:

Temperature	Wavelength Limits, 5% to 90%
1000K	1.88 – 9.4 μm
2000K	0.94 – 4.7
3000K	0.63 – 3.1

Material	Temperature	$\epsilon_{0.65\mu m}$	λ_{sw}	λ_{lw}	ϵ_t
Ni	1500	0.39	1.2	6.3	?
Zr	2000	0.35	0.9	4.7	?
Au	1400	0.25	1.3	6.7	?
Ni-Zr	1200	?	1.6	7.8	?
Ag	1200	0.06	1.6	7.8	?

FOUR-DETECTOR POLARIMETRY

* Combination of Polarimetry and Radiometry.

* No moving parts.

* Complete Polarization State measured in < 10 ms.

* Distinguishes between Circular and Unpolarized light.

* Rejects unpolarized light.

* Insensitive to illumination uniformity.

* Imaging.

* Easy setup and alignment (automated).

POLARIZATION STATE DETECTOR (PSD)

Reference
Detector

POLARIZATION STATE GENERATOR (PSG)

Chopper   Polarizer

Unpolarized
HeNe Laser

Quarter
Wave
Retarder

Stepper
Motor
Controller

Pellicle
Membrane

Pellicle
Membrane

Beam Splitting
Glan Thompson

Coated
Beamsplitter

D_1

D_0

I_1

I_0

D_3

D_2

I_3

I_2

Quadrant
Detector

Mirror

Switch

Computer

A to D
Card

Signal Processing
Module

Polarimetric Analysis

The Stokes parameters are related to the azimuth α and ellipticity χ of the polarized component, the degree of polarization p, and the overall intensity I of the light received by the PSD as follows:

$$S_o = I \tag{1a}$$

$$S_1 = S_o \, p \, \cos(2\chi) \, \cos(2\alpha) \tag{1b}$$

$$S_2 = S_o \, p \, \cos(2\chi) \, \sin(2\alpha) \tag{1c}$$

$$S_3 = S_o \, p \, \sin(2\chi) \tag{1d}$$

The inverse relationship between the polarimetric parameters α, χ, and p to the Stokes parameters are:

$$p = \frac{\sqrt{S_1^2 + S_2^2 + S_3^2}}{S_0} \tag{2a}$$

$$\alpha = \frac{1}{2} \tan^{-1}\left[\frac{S_2}{S_1}\right] \tag{2b}$$

$$\chi = \frac{1}{2} \tan^{-1}\left[\frac{S_3}{\sqrt{S_1^2 + S_2^2}}\right] \tag{2c}$$

MEASUREMENT OF STOKES PARAMETERS

INCOMING LIGHT HAS STOKES VECTORS:

$$S = [\ S_0\ S_1\ S_2\ S_3\ ]^T, \text{ WHERE T STANDS FOR THE TRANSPOSE.}$$

THE FOUR MEASURED VOLTAGES (INTENSITIES) ARE:

$$I = [\ I_0\ I_1\ I_2\ I_3\ ]^T.$$

THESE ARE RELATED THROUGH THE INSTRUMENT MATRIX M (4 X 4) THAT TRANSFORMS INCOMING STOKES VECTORS INTO MEASURED INTENSITIES.

$$I = M\ S$$

THE UNKNOWN STOKES VECTOR IS CALCULATED FROM:

$$S = M^{-1}\ I$$

THE INSTRUMENT MATRIX, M, IS OBTAINED BY ILLUMINATING THE POLARIMETER WITH A SET OF LINEARLY INDEPENDENT, KNOWN STOKES VECTORS:

$$M_{inst} = \begin{bmatrix} 0.502 & -0.232 & 0.143 & 0.088 \\ 0.576 & -0.293 & -0.169 & -0.142 \\ 0.737 & 0.333 & 0.634 & 0.108 \\ 0.693 & 0.310 & -0.600 & -0.079 \end{bmatrix}$$

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Ellipsometry

o   If $\Psi_0 = 45°$, and the reflected light Stokes parameters are measured, then the fundamental ellipsometric parameters, Ψ, and Δ, are given by:

$$\psi = \tan^{-1} \frac{\sqrt{S_2^2 + S_2^3}}{-S_1} \tag{3a}$$

$$\Delta = \tan^{-1}\left(\frac{-S_3}{S_2}\right) \tag{3b}$$

o   Governing equations:

$$\rho = \tan(\psi) \, e^{i\Delta}$$

o   Ellipsometric measurements allow one to measure:

n_2, k_2 = substrate n and k values.
n_1 = film refractive index.
d_f = film thickness.

o   For a bare substrate:

$$n_2 - ik_2 = \tan\phi \left[1 - \frac{4\rho}{(1 + \rho)^2} \sin^2\phi \right]^{\frac{1}{2}}$$

For a film on a substrate of known properties (eg. **in vitro**)

n_1, d_f == $f\left(\Psi, \Delta, n_2, k_2, \theta \right)$

o   Spectroscopic ellipsometry allows multi-layer films to be analyzed.

**TABLE I.   POLARIMETRIC AND RADIOMETRIC
CHARACTERISTICS OF LEAP AT 632.8 nm**

QUANTITY	ERROR
S_1	0.009
S_2	0.010
S_3	0.008
PHASE, Δ	0.05·
AZIMUTH, α	0.05·
ELLIPTICITY, χ	0.05·
AXIAL RATIO	0.05·
DEGREE OF POLARIZATION, P	0.5%
DEGREE OF LINEAR POLARIZATION	0.8%
DEGREE OF CIRCULAR POLARIZATION	0.4%
INDEX OF REFRACTION, N	0.016
EXTINCTION COEFFICIENT, K	0.02
NORMAL SPECTRAL EMISSIVITY, E	0.002
TEMPERATURE ACCURACY @ 2100 K	3 K
TEMPERATURE RESOLUTION @ 2100 K	2 K
RESPONSE TIME	25 ms

MELTING POINT MEASUREMENTS ON Zirconium

Emissivity Measurements:

* ϵ (0.632 μm) = 0.351, DAPP measurements

* ϵ (0.650 μm) = 0.367
    A. Cezairliyan and F. Righini, Rev. Int. Htes. Temp. et Refract., 12, 201-207 (1975).

* ϵ (0.632 μm) = 0.345 $\pm$ 0.002, RAE measurements

Apparent Melting Temperatures:

* T_a = 1928 $\pm$ 2 K, DAPP measurements

* T_a = 1927 $\pm$ 2 K, Vanderbilt University

* T_a = 1940 $\pm$ 2 K, A. Cezairliyan and F. Righini

* T_a = 1928 $\pm$ 2 K, Calibrated Pyrometer measurements

True Melting Point:

* T_m = 2125 $\pm$ 11 K, our measurements

* T_m = 2128 $\pm$ 8 K, A. Cezairliyan and Righini

* T_m = 2125 $\pm$ 15 K, JANAF Thermochemical tables

Session III

Theoretical Predictions